

alkylbenzene

PATENT ABSTRACTS OF JAPAN

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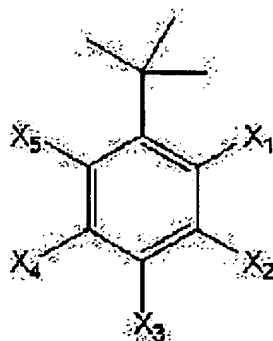
(54) NON-ACQUEOUS ELECTROLYTE AND LITHIUM SECONDARY BATTERY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery having excellent battery characteristics such as cycle characteristic and electric capacity of the battery and storage characteristic.

SOLUTION: In non-aqueous electrolyte prepared by dissolving electrolyte in non-aqueous solvent, the non-aqueous electrolyte contains tert-butylbenzene derivative expressed by the following formula (I):

(wherein, X1, X2, X3, X4, and X5 denote hydrogen atom or halogen atom independently, respectively, and at least one of X1 to X5 is halogen atom), and the lithium secondary battery using the non-aqueous electrolyte is provided.



(1)

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte which can offer the lithium secondary battery excellent also in cell properties, such as the cycle property of a cell, and electric capacity, a preservation property, and the lithium secondary battery using it.

[0002]

[Description of the Prior Art] In recent years, the lithium secondary battery is widely used as power sources for a drive, such as small electronic equipment. The lithium secondary battery mainly consists of a positive electrode, nonaqueous electrolyte, and a negative electrode, and the lithium secondary battery which used lithium multiple oxides, such as LiCoO_2 , as the positive electrode, and used the carbon material or the lithium metal as the negative electrode is used especially suitably. And as nonaqueous electrolyte for the lithium secondary batteries, carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and methylethyl carbonate (MEC), is used suitably.

[0003]

[Problem(s) to be Solved by the Invention] However, the rechargeable battery which has the further excellent property about cell properties, such as the cycle property of a cell and electric capacity, is called for. When the solvent in nonaqueous electrolyte carries out oxidative degradation of the part locally at the time of charge, the lithium secondary battery using LiCoO_2 , LiMn_2O_4 , LiNiO_2 , etc. as a positive electrode produces cell performance degradation, in order that this decomposition product may check the desirable electrochemical reaction of a cell. This is considered to originate in the electrochemical oxidation of the solvent in the interface of a positive-electrode ingredient and nonaqueous electrolyte. Moreover, while the lithium secondary battery using high-crystallized carbon materials, such as a natural graphite and an artificial graphite, repeats charge and discharge also in EC for which the solvent in nonaqueous electrolyte carries out reduction decomposition on a negative-electrode front face at the time of charge, and is generally widely used as a nonaqueous electrolyte solvent at it as a negative electrode, reduction decomposition takes place in part, and cell performance degradation happens. For this reason, the present condition is that cell properties, such as the cycle property of a cell and electric capacity, are not necessarily satisfactory.

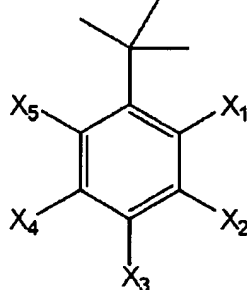
[0004] This invention aims at offering the nonaqueous electrolyte for lithium secondary batteries which can constitute the lithium secondary battery which solved the technical problem about the above nonaqueous electrolyte for lithium secondary batteries, was excellent in the cycle property of a cell, and was further excellent also in cell properties, such as electric capacity and a preservation property in a charge condition, and the lithium secondary battery using it.

[0005]

[Means for Solving the Problem] It sets to the nonaqueous electrolyte by which the electrolyte is dissolved in the non-aqueous solvent, and this invention is the following type (I) in this nonaqueous electrolyte.

[0006]

[Formula 3]

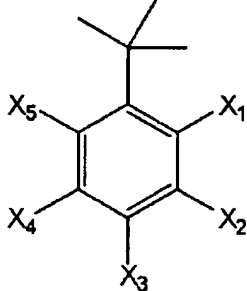


(I)

[0007] (-- X₁, X₂, X₃, X₄, and X₅ show independently a hydrogen atom or a halogen atom among a formula, respectively, and at least one of X₁-X₅ is a halogen atom.) -- it is related with the nonaqueous electrolyte characterized by the tert-butylbenzene derivative expressed containing. Moreover, it sets to the lithium secondary battery which consists of nonaqueous electrolyte by which the electrolyte is dissolved in the positive electrode, the negative electrode, and the non-aqueous solvent, and is the following type (I) in this nonaqueous electrolyte.

[0008]

[Formula 4]



(I)

[0009] (-- X₁, X₂, X₃, X₄, and X₅ show independently a hydrogen atom or a halogen atom among a formula, respectively, and at least one of X₁-X₅ is a halogen atom.) -- it is related with the lithium secondary battery characterized by the tert-butylbenzene derivative expressed containing.

[0010] The nonaqueous electrolyte of this invention is used as a configuration member of a lithium secondary battery. Especially about configuration members other than the nonaqueous electrolyte which constitutes a rechargeable battery, it is not limited but the various configuration members currently used conventionally can be used.

[0011]

[Embodiment of the Invention] In the tert-butylbenzene derivative expressed with said general formula (I) contained in the nonaqueous electrolyte by which the electrolyte is dissolved in the non-aqueous solvent, X₁, X₂, X₃, X₄, and X₅ are a hydrogen atom or a halogen atom independently, respectively. As a halogen atom, a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom is desirable.

[0012] As an example of a tert-butylbenzene derivative expressed with said general formula (I) For example, a 1-tert-butyl-4-fluorobenzene [X₁=X₂=X₄=X₅= hydrogen atom, X₃= fluorine atom], a 1-tert-butyl-4-chlorobenzene [X₁=X₂=X₄=X₅= hydrogen atom, X₃= chlorine atom], a 1-BUROMO-2-tert-butylbenzene [X₂=X₃=X₄=X₅= hydrogen atom, X₁= bromine atom], a 1-BUROMO-3-tert-butylbenzene [X₁=X₃=X₄=X₅= hydrogen atom, X₂= bromine atom], a 1-BUROMO-4-tert-butylbenzene [X₁=X₂=X₄=X₅= hydrogen atom, X₃= bromine atom], 1-tert-butyl - 3 Five - A dibromo benzene [X₁=X₃=X₅= hydrogen atom and X₂=X₄= bromine atom] 1-tert-butyl-4-iodobenzene [a X₁=X₂=X₄=X₅= hydrogen atom and X₃= iodine atom] etc. is mentioned.

[0013] If there are too many contents of the tert-butylbenzene derivative expressed with said formula (I) contained in nonaqueous electrolyte, sufficient cell engine performance which the cell engine

performance may fall and was expected to be too few will not be obtained. Therefore, since the cycle property of range [0.5 - 5% of the weight of] improves preferably especially 0.2 to 10% of the weight 0.1 to 20% of the weight to the weight of nonaqueous electrolyte, the content is good.

[0014] As a non-aqueous solvent used by this invention, what consists of a high dielectric constant solvent and a hypoviscosity solvent is desirable. As a high dielectric constant solvent, annular carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC), is mentioned suitably, for example. These high dielectric constant solvents may be used by one kind, and they may be used, combining them two or more kinds.

[0015] As a hypoviscosity solvent, for example Dimethyl carbonate (DMC), methylethyl carbonate (MEC), Chain-like carbonate, such as diethyl carbonate (DEC), a tetrahydrofuran, 2-methyl tetrahydrofuran, 1,4-dioxane, 1, 2-dimethoxyethane, Ether, such as 1, 2-diethoxy ethane, 1, and 2-dibutoxy ethane, Amides, such as ester, such as nitril, such as lactone, such as gamma-butyrolactone, and an acetonitrile, methyl propionate, pivalate methyl, and pivalate octyl, and dimethylformamide, are mentioned. These hypoviscosity solvents may be used by one kind, and they may be used, combining them two or more kinds. A high dielectric constant solvent and a hypoviscosity solvent are chosen as arbitration, respectively, and are combined and used. in addition, an aforementioned high dielectric constant solvent and an aforementioned hypoviscosity solvent -- a capacity factor (high dielectric-constant solvent: hypoviscosity solvent) -- usually -- 1:9-4:1 -- 1:4-7:3 come out comparatively preferably, and it is used.

[0016] As an electrolyte used by this invention, for example LiPF_6 , LiBF_4 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ and $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiPF}_4(\text{CF}_3)_2$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$, $\text{LiPF}_3(\text{CF}_3)_3$, $\text{LiPF}_3(\text{iso-C}_3\text{F}_7)_3$, $\text{LiPF}_5(\text{iso-C}_3\text{F}_7)$, etc. are mentioned. These electrolytes may be used by one kind, and they may be used, combining them two or more kinds. 0.1-3 M of these electrolytes is usually preferably used by the concentration of 0.5-1.5M, dissolving in the aforementioned non-aqueous solvent.

[0017] The nonaqueous electrolyte of this invention is obtained by mixing an aforementioned high dielectric constant solvent and an aforementioned hypoviscosity solvent, dissolving the aforementioned electrolyte in this, and dissolving the tert-butylbenzene derivative expressed with said formula (I).

[0018] For example, the compound metallic oxide of the at least one kind of metal and the lithium which are chosen from the group which consists of cobalt, manganese, nickel, chromium, iron, and vanadium as positive active material is used. As such a compound metallic oxide, LiCoO_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, etc. are mentioned, for example. Only one kind may be chosen and used for such positive active material, and may be used for it combining two or more kinds.

[0019] A positive electrode the aforementioned positive active material Electric conduction agents, such as acetylene black and carbon black, Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), The copolymer (SBR) of styrene and a butadiene, the copolymer of acrylonitrile and a butadiene (NBR), After considering as a mixture, this positive-electrode ingredient is applied to the lath plate of the aluminium foil as a charge collector, or the product made from stainless steel. binders, such as a carboxymethyl cellulose (CMC), and a solvent -- kneading -- a positive electrode -- It is produced after desiccation and pressurization molding by heat-treating under a vacuum at the temperature of 50 degrees C - about 250 degrees C for about 2 hours.

[0020] Matter, such as a carbon material [the pyrolytic carbon, the corks, the graphite, the organic high-molecular-compounds (artificial-graphite, natural graphite, etc.) combustion object, and the carbon fiber] or a compound stannic-acid ghost which has the graphite mold crystal structure which can emit [occlusion and] a lithium metal, a lithium alloy, or a lithium as a negative-electrode active material, is used. It is desirable to use the carbon material which has especially the graphite mold crystal structure whose spacing (d_{002}) of a lattice plane (002) is 0.335-0.340nm. Only one kind may be chosen and used for these negative-electrode active materials, and may be used for them combining two or more kinds. in addition, a powder ingredient like a carbon material -- binders, such as a copolymer (SBR) of an ethylene-propylene-diene terpolymer (EPDM), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), styrene, and a butadiene, a copolymer (NBR) of acrylonitrile and a butadiene, and a carboxymethyl cellulose (CMC), -- kneading -- a negative electrode -- it is used as a mixture. Especially

the manufacture approach of a negative electrode is not limited, but can be manufactured by the manufacture approach of the above-mentioned positive electrode, and the same approach.

[0021] Especially the structure of a lithium secondary battery is not limited and the positive electrode of a monolayer or a double layer, a negative electrode, the coin mold cell which has a separator and a polymer battery, a cylindrical cell, a square shape cell that has the separator of the shape of a roll-like positive electrode, a negative electrode, and a roll further, etc. are mentioned as an example. In addition, the fine porosity film of polyolefine well-known as a separator, textile fabrics, a nonwoven fabric, etc. are used.

[0022]

[Example] Next, an example and the example of a comparison are given and this invention is explained concretely.

after preparing the non-aqueous solvent of example 1 [preparation of nonaqueous electrolyte]

EC:PC:DEC(capacity factor) =30:5:65, dissolving so that it may become the concentration of 1M about LiPF₆ at this, and preparing nonaqueous electrolyte -- further -- 1-BUROMO-4-tert-butylbenzene was added so that it might become 2.0 % of the weight to nonaqueous electrolyte.

[0023] [Production of a lithium secondary battery and measurement of a cell property] What mixed acetylene black (electric conduction agent) 10% of the weight 80% of the weight, mixed polyvinylidene fluoride (binder) at 10% of the weight of a rate, added the 1-methyl-2-pyrrolidone solvent to this, and was mixed was applied on aluminium foil, it dried, LiCoO₂ (positive active material) was pressurization-cast, it heat-treated, and the positive electrode was prepared. It dried and pressurization-cast, applied what mixed the artificial graphite (negative-electrode active material) 90% of the weight, mixed polyvinylidene fluoride (binder) at 10% of the weight of a rate, added the 1-methyl-2-pyrrolidone solvent to this, and was mixed on copper foil and heat-treated, and the negative electrode was prepared. And using the separator of a polypropylene fine porosity film, the above-mentioned nonaqueous electrolyte was made to pour in and the coin cell (3.2mm in the diameter of 20mm, thickness) was produced. Using this coin cell, under the room temperature (20 degrees C), it charged to termination electrical-potential-difference 4.2V for 5 hours, and then discharged to termination electrical-potential-difference 2.7V under 0.8mA constant current, and this charge and discharge were repeated by 0.8mA constant current and the constant voltage. Initial charge-and-discharge capacity is 4-tert-butylbenzene derivative additive-free 1M. It was 1.03 in the relative value which set to 1 the case (example 1 of a comparison) where LiPF₆-EC/PC/DEC (capacity factor 30/5/65) was used as nonaqueous electrolyte, and when the cell property after 50 cycles was measured, the discharge capacity maintenance factor when making initial discharge capacity into 100% was 92.4%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0024] When used example 21-BUROMO-4-tert-butylbenzene 5.0% of the weight to nonaqueous electrolyte, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the discharge capacity maintenance factor was 91.9%. The production conditions and cell property of a coin cell are shown in Table 1.

[0025] When used 1-BUROMO-4-tert-butylbenzene 0.5% of the weight to nonaqueous electrolyte as example 3 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the discharge capacity maintenance factor was 91.3%. The production conditions and cell property of a coin cell are shown in Table 1.

[0026] The non-aqueous solvent of example of comparison 1 EC:PC:DEC(capacity factor) =30:5:65 was prepared, and it dissolved so that it might become the concentration of 1M about LiPF₆ at this. At this time, the tert-butylbenzene derivative was not added at all. The coin cell was produced like the example 1 using this nonaqueous electrolyte, and the cell property was measured. The discharge capacity maintenance factor after 50 cycles was 82.6% to initial discharge capacity. The production conditions and cell property of a coin cell are shown in Table 1.

[0027] after preparing the non-aqueous solvent of example 4 EC:PC:DEC(capacity factor) =30:5:65, dissolving so that it may become the concentration of 1M about LiPF₆ at this, and adjusting nonaqueous electrolyte -- further -- the 1-tert-butyl-4-iodobenzene was added so that it might become 2.0 % of the

weight to nonaqueous electrolyte. The place which produced the coin cell like the example 1 using this nonaqueous electrolyte, and measured the cell property, Initial discharge capacity is 4-tert-butylbenzene derivative additive-free 1M. It is 1.02 in the relative value which set to 1 the case (example 1 of a comparison) where LiPF₆-EC/PC/DEC (capacity factor 30/5/65) was used as nonaqueous electrolyte. When the cell property after 50 cycles was measured, the discharge capacity maintenance factor when making initial discharge capacity into 100% was 92.1%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0028] As example 5 nonaqueous electrolyte, it is 1M. When used LiPF₆-EC/PC/MEC/DMC (capacity factor 30/5/50/15), replaced with LiCoO₂, and used LiNi_{0.8}Co_{0.2}O₂ as positive active material, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the discharge capacity maintenance factor was 91.1%. The production conditions and cell property of a coin cell are shown in Table 1.

[0029] As example 6 nonaqueous electrolyte, it is 1M. When used LiBF₄-EC/PC/DEC/DMC (capacity factor 30/5/30/35), replaced with LiCoO₂, and used LiMn₂O₄ as positive active material, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the discharge capacity maintenance factor was 92.5%. The production conditions and cell property of a coin cell are shown in Table 1.

[0030]

[Table 1]

	正極	負極	化合物	添加量 wt%	電解液組成 (容量比)	初期 放電容量 (相対値)	50サイ クル 放電容量 維持率%
実施例 1	LiCoO ₂	人造 黒鉛	1-ブromo-4-tert- ブチルベンゼン	2.0	1M LiPF ₆ EC/PC/DEC=30/5/65	1.03	92.4
実施例 2	LiCoO ₂	人造 黒鉛	1-ブromo-4-tert- ブチルベンゼン	5.0	1M LiPF ₆ EC/PC/DEC=30/5/65	1.02	91.9
実施例 3	LiCoO ₂	人造 黒鉛	1-ブromo-4-tert- ブチルベンゼン	0.5	1M LiPF ₆ EC/PC/DEC=30/5/65	1.01	91.3
比較例 1	LiCoO ₂	人造 黒鉛	なし	0	1M LiPF ₆ EC/PC/DEC=30/5/65	1.00	82.6
実施例 4	LiCoO ₂	人造 黒鉛	1-tert-ブチル-4- ヨードベンゼン	2.0	1M LiPF ₆ EC/PC/DEC=30/5/65	1.02	92.1
実施例 5	LiNi _{0.8} Co _{0.2} O ₂	人造 黒鉛	1-ブromo-4-tert- ブチルベンゼン	2.0	1M LiPF ₆ EC/PC/MEC/DMC =30/5/50/15	1.15	91.1
実施例 6	LiMn ₂ O ₄	人造 黒鉛	1-ブromo-4-tert- ブチルベンゼン	2.0	1M LiBF ₄ EC/PC/DEC/DMC =30/5/30/35	0.99	92.5

[0031] In addition, this invention is not limited to the example of a publication, but various combination which can be guessed is easily possible for it from the meaning of invention. Especially the combination of the solvent of the above-mentioned example is not limited. Furthermore, although the above-mentioned example is related with a coin cell, this invention is applied also to the cell of a cylindrical shape and a prism form.

[0032]

[Effect of the Invention] According to this invention, the lithium secondary battery excellent in cell properties, such as the cycle property of a cell, electric capacity, and a preservation property, can be offered.

[Translation done.]